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GASEOUS DIFFUSION IN GLASSY POLYMERS*

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Dedicated to Joseph Keller

Abstract. A model for gaseous diffusion in glassy polymers is developed with a view to accounting for the observations made in dual sorption and certain other phenomena in polymers below their glass transition temperature. In this paper a preliminary study of the effects of both the immobilizing mechanism and the generalized diffusion mechanism on travelling waves and the diffusive wavefronts is made.

1. Introduction. In the period 1953–1969 a partially successful chemical and mathematical theory was developed for the diffusion behavior of glassy polymers and the transition between rubbery and glassy states. Good summaries of this development are given in Crank [1] and Crank and Park [2]. While it was recognized at the time that many fundamental chemical mechanisms were still unknown, and also that the corresponding mathematical theory was inadequate due to its inherent and often ignored nonlinearity, nevertheless combinations of gross qualitative chemical theories and crude linearizations plus numerical studies gave acceptable answers for the problems of the time [2]. However, recent technological discoveries lead to a variety of new problems far exceeding the capabilities of the previously developed theories. Among these are problems in the disposal of chemical waste, the structural failure of plastics and polymers, the replacement of traditional materials by polymers, the development of barriers (e.g., plastic beverage bottles) to separate gas mixtures, the migration of impurity atoms in solids which should be ultra-pure for their use in solid-state electronic devices, and the role of diffusion in catalysis by porous solids.

Roughly speaking, the major effects depend upon whether the polymer is above (rubbery) or below (glassy) its glass transition temperature and whether the penetrant is a liquid or a gas, but this is only a crude over-simplification. A polymer in its rubbery state responds rapidly (almost instantaneously) to changes in its condition. This has many simplifying implications, and it is now universally agreed [1], [3] that diffusion in rubbery polymers is described by the standard Fickian diffusion equation $C_t = \text{div}\,(D\ \text{grad}\ C)$, in which the diffusivity D is at worst dependent upon the concentration C of the diffusing species; i.e., $D = D(C)$. Although problems involving this equation may be formidable nonlinear boundary value problems, the important qualitative features of diffusion in rubbery polymers can be obtained, and indeed, a rather complete theory [1] exists.

On the other hand, there is no unifying theoretical formulation for glassy polymers. There is not even a complete classification of the various anomalous effects. Glassy polymers respond slowly to changing conditions, and most of the anomalous effects are directly related to this. For example, the changing polymer structure influences the solubility and diffusional mobility. This leads to diffusion coefficients which can depend not only nonlinearly on the state of the system, but also on the previous history of the system, and sometimes even on previous rates of change of the system [1], [4]. Internal stresses can be induced due to differential swelling of different parts of the polymer [5]–[7]. Immobilization (and sometimes reaction) in the interstitial

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spaces and microvoids greatly affects the sorption of diffusing penetrants [8]–[10]. These and many other phenomena have given rise to a partial classification (Case II, Super-case II, dual-mode, anomalous non-Fickian, . . .) of glassy polymers according to various experimental observations. Indeed, the observations are sometimes so diverse that, rather than any kind of universal theory for glassy polymers it is probably the case that theories of glassy polymers by still to be defined type will be all that is obtainable. In any event, many more studies of special problems are necessary before some more or less global theory can be proposed.

In this paper we shall study the general problem of dual sorption in glassy polymers. We shall be more precise in § 2 where we present the equations of motion, but roughly speaking dual sorption involves two distinct mechanisms: (i) ordinary diffusion controlled sorption, and (ii) sorption resulting from the immobilization (or partial immobilization) of diffusing gas molecules by various sites in the polymer [9]. These sites are interstitial spaces and microvoids which are consequences of local heterogeneities, and which are intimately related to the slow relaxation processes associated with the glassy state of the polymer (probably close to the glass transition temperature).

We shall study systems of equations of the form

$$C_t = (DC_x)_x + R(C), \tag{1.1}$$

$$D_t = F'(C)C_t + \alpha(C)[G(C) - D], \tag{1.2}$$

and certain natural generalizations of this system for which the theories of Vieth and Sladek [8], Tshudy and von Frankenberg [9], Paul and Koros [10], and Petropoulos [11] are all special cases. Diffusion operators with diffusivity changing according to (1.2) were first proposed by Crank [1], [12] to account for totally different observations involving swelling when a liquid penetrant diffuses into a glassy polymer. Crank's arguments are cogent, and appropriate generalizations are broadly applicable to large classes of generalized diffusion problems. In § 2 we shall show how to obtain the standard dual mode sorption theories [8]–[11] from a generalization of Crank's model. In addition, we show that our model then unifies dual mode sorption with certain parts of the so-called Case II, Super-case II, and anomalous non-Fickian phenomena.

Because of the relative ease with which it can be obtained, both experimentally and theoretically, the single quantity most commonly used to define the kinetics of the sorption process [7] is

$$M_t = kt^n, \tag{1.3}$$

where M_t is the total amount of penetrant absorbed per unit area of polymer at time t, and k and n are system parameters. Standard Fickian diffusion (i.e., a polymer in its rubbery state above the glass transition temperature) corresponds to the usual $n = \frac{1}{2}$. Case II glassy polymers correspond to $\frac{1}{2} \leqq n \leqq 1$, and Super-case II corresponds to $n > 1$. However, this is not a hard and fast rule, and furthermore, in most glassy polymers M_t as a function of t does not look like t^n for one constant value of n. In dual mode sorption and in anomalous non-Fickian cases the most commonly observed function for M_t is what is now universally called "sigmoid" by polymer chemists [1], [3]. That is, M_t as a function of t commonly exhibits a single point of inflection (most often at about 50% of equilibrium sorption). For example, in the penetration of cellulose acetate by acetone vapor [13], M_t versus $t^{1/2}$ is linear for both small and large time t joined for intermediate time by a curve with a single inflection point. The

penetration of polystyrene by methane [14] exhibits an M_t versus t with two linear regions connected by a nonlinear region.

This sigmoid absorption behavior can be controlled by either the diffusivity D or the kinetic-like term $R(C)$ in (1.1), (1.2). The following simple heuristic arguments give a feeling for the mechanisms involved: The function $\alpha(C)$ in (1.2) is a rate controlling function (empirically obtained) depending monotonically on C. From (1.2) it is clear that large α implies $D \sim G(C)$, the equilibrium diffusion coefficient, and small α implies $D \sim F(C)$, the instantaneous diffusion coefficient. (Note that in either state the concentration in an absorption process is increasing.) For intermediate values of α the diffusion coefficient D is history dependent (we shall show this in § 2), and it is this transition from small to large values of α which accounts for the so-called sigmoid absorption curve. We shall demonstrate this more explicitly in § 5 where we employ a Karman–Pohlhausen integral averaging method to obtain the time history of the penetration front.

The term $R(C)$ in (1.1) arises from a consideration of one or a combination of the following phenomena: (i) The immobilization of some diffusing molecules simply by filling voids, (ii) the immobilization (or partial immobilization) of some diffusing molecules by absorption at specific sites, or (iii) the intraconversion of two or more differently mobile penetration species. Equilibrium states exist in all these situations, and as we shall see, since the most commonly occurring form for $R(C)$ is a bimolecular rate function, then two equilibrium states usually exist. The sigmoid absorption behavior is manifested by a diffusion wave connecting these states. We prove the existence of these waves in § 3 and construct them via a perturbation scheme in a special case in § 4.

2. Dual sorption theory. Experimental results readily show that the sorption isotherms for gases such as CO_2, CH_4, and C_2H_6 in glassy polymers such as ethylene terephthalate and polystyrene are nonlinear [10], [14]–[16] and can best be described by a function of the form

$$C = \alpha p + \frac{\beta p}{1+\gamma p}, \tag{2.1}$$

where C is the equilibrium concentration of gas in the polymer, p is the pressure, and α, β, and γ are various physical constants. It is standard [8]–[10], [14]–[16] to write (2.1) in the form

$$C = C_D + C_H, \tag{2.2}$$

where

$$C_D = \alpha p, \qquad C_H = \frac{\beta p}{1+\gamma p}, \tag{2.3}$$

and to interpret (2.2) as implying that two separate sorption mechanisms are operating: (i) Standard linear sorption in which C_D denotes the gas dissolved according to Henry's law (i.e., $C_D = \alpha p$), and (ii) hole filling (or immobilization) in which C_H denotes gas adsorbed into holes according to a Langmuir-type isotherm (i.e., $C_H = \beta p/(1+\gamma p)$). Note that C is linear in p for both small and large p; i.e.,

$$C \sim (\alpha+\beta)p \quad \text{for small } p, \tag{2.4}$$

$$C \sim \alpha p + \frac{\beta}{\gamma} \quad \text{for large } p. \tag{2.5}$$

This behavior, (2.4), (2.5), of two linear regions with a connecting nonlinear region is the typical experimental observation [8], [14] noted for gaseous diffusion in a glassy polymer.

In the theories assuming complete immobilization [8], [10] of the gas adsorbed in the holes one assumes that only the dissolved gas is free to diffuse so that (neglecting convection) the flux J of diffusing gas is given by

$$J = -D\frac{\partial C_D}{\partial x}, \tag{2.6}$$

where D is the diffusion coefficient of the dissolved penetrant. (For algebraic simplicity we shall stick to one dimension. The multi-dimensional derivation in which J is proportional to the gradient of C is easy to carry out.) The basic equation of continuity (i.e., conservation of mass) then becomes

$$\frac{\partial C}{\partial t} = \frac{\partial}{\partial t}(C_D + C_H) = -\frac{\partial J}{\partial x}. \tag{2.7}$$

Local equilibrium between C_D and C_H implies that at any position the pressure is the same for both species. Thus, since $p = C_D/\alpha$, we have

$$C_D + C_H = C_D + \frac{(\beta/\alpha)C_D}{1+(\gamma/\alpha)C_D}. \tag{2.8}$$

Hence,

$$\frac{\partial}{\partial t}\left(C_D + \frac{(\beta/\alpha)C_D}{1+(\gamma/\alpha)C_D}\right) = \frac{\partial}{\partial x}\left(D\frac{\partial C_D}{\partial x}\right), \tag{2.9}$$

or equivalently,

$$\left[1 + \frac{\beta/\alpha}{(1+(\gamma/\alpha)C_D)^2}\right]\frac{\partial C_D}{\partial t} = \frac{\partial}{\partial x}\left(D\frac{\partial C_D}{\partial x}\right). \tag{2.10}$$

The derivation of (2.10) can be carried out in a more sophisticated manner [10]–[11] by using various thermodynamic arguments and invoking a flux driven by gradients of a chemical potential rather than a concentration. This allows one to relax the assumption of complete immobilization and use instead the concept of partial immobilization of some gas molecules due to several possible mechanisms [1]. Nevertheless, the form of (2.10) remains the same with only slight modification in the specific constants and functional forms of the coefficients in (2.10).

A totally different formulation of the dual sorption implied by (2.2) is presented by Tshudy and von Frankenberg [9]. They assume that there are a fixed number of immobilizing sites distributed uniformly throughout the polymer and that each site can immobilize only one gas molecule according to some mechanism whose effect can be written as

$$\text{site} + \text{gas molecule} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \text{site molecule complex}. \tag{2.11}$$

By writing the specific function R describing the "reaction" (2.11) and by invoking ordinary diffusion they then write the basic continuity equation as

$$\frac{\partial C_D}{\partial t} = \frac{\partial}{\partial x}\left(D\frac{\partial C_D}{\partial t}\right) + R. \tag{2.12}$$

Partial immobilization can be accounted for through the use of a reversible reaction (2.11), and the effective rate constants k_1 and k_{-1} can be adjusted to yield the same equilibrium sorption isotherms as the other theories which start with (2.10).

In a different context, involving swelling of the polymer structure due to (mostly liquid) penetrants, Crank [1], [12] proposed a phenomenological approach which we now generalize to the present problem of dual sorption. This generalization embodies all of the above theories. Crank proposed the system

$$\frac{\partial C}{\partial t} = \frac{\partial}{\partial x}\left(D\frac{\partial C}{\partial x}\right), \tag{2.13}$$

$$\frac{\partial D}{\partial t} = F'(C)\frac{\partial C}{\partial t} + \alpha(C)[G(C) - D]. \tag{2.14}$$

He presents simple convincing arguments, which we summarized in § 1, to interpret $F(C)$ as an instantaneous diffusion coefficient reflecting instantaneous changes in the polymer, $G(C)$ as an equilibrium diffusion coefficient reflecting the slow relaxation due to its glassy state, and $\alpha(C)$ as a rate function controlling the approach to equilibrium. Crank further points out that (2.14) implies that the diffusivity D depends not only on the concentration, but also on the time taken to reach that concentration, and thus, some previous history is also incorporated into (2.14).

Basic to all the theories mentioned above is the explicit assumption of a diffusion mechanism taking account of the relatively slow relaxation of a polymer in its glassy state. This mechanism is superposed on the usual classical diffusion in such a way that the total diffusion process models the experimental observations that at low concentration (and/or pressure) the process acts as a classical (i.e., Fickian) diffusion process with one (possibly concentration dependent) diffusion coefficient, and at high concentration (and/or pressure) the process acts the same way but with a different diffusion coefficient. These regimes are connected by a nonlinear region in which the dominant behavior is due to adjusting to the changing polymer structure (for example, the process of filling microvoids by the binding or immobilizing of some of the diffusion gas). With this observation it is clear that Crank's diffusion mechanism (2.13), (2.14) has the proper ingredients for describing the evolving diffusivity. In addition, lacking detailed knowledge of the complex physical and chemical processes taking place in the interstitial spaces, we can incorporate all possible processes in a general relation (2.11) of the Tshudy–von Frankenberg type. There is no need at this state to make specific assumptions on the distribution of sites or the process at each site, and we incorporate the observations that these complex processes depend on the rate of change and the local flux of the concentration. Thus, we propose

$$\frac{\partial C}{\partial t} = \frac{\partial}{\partial x}\left(D\frac{\partial C}{\partial x}\right) + R(x, t, C, C_t, C_x), \tag{2.15}$$

$$\frac{\partial D}{\partial t} = F'(C)\frac{\partial C}{\partial t} + \alpha(C)[G(C) - D], \tag{2.16}$$

where $R(x, t, C, C_t, C_x)$ represents the (at this stage unknown) kinetics implied by the process (2.11).

Note that (2.16) can be integrated to express D as

$$D = D_0 \exp\left(-\int_0^t \alpha(C(x,\tau))\,d\tau\right) + \int_0^t \exp\left(-\int_s^t \alpha(C(x,\tau))\,d\tau\right)[F'(C(x,s))C_t(x,s) + \alpha(C(x,s))G(C(x,s))]\,ds, \tag{2.17}$$

where $D_0 = D$ at $t = 0$. In this form we see explicitly the history dependence of D represented as an integral over time with a kernel

$$\exp\left(-\int_s^t \alpha(C(x,\tau))\,d\tau\right). \tag{2.18}$$

This kernel represents the delay (or heredity) inherent in the relaxation process. Progressing along these lines, we can replace (2.16) or (2.17) with the more general assumption that

$$D = \int_0^t K(t, s, C(x,s))f(C(x,s), C_t(x,s))\,ds \tag{2.19}$$

with an appropriate (hereditary or delay) kernel $K(t, s, C)$ and an appropriate concentration dependent f. The system consisting of (2.15) and (2.19) provides an appealing model for describing dual sorption and certain parts of the so-called Case II, Super-case II, and anomalous non-Fickian phenomena. Most of the current models are special cases of (2.15), (2.19). Thus, (2.15), (2.19) provides a unifying theory which so far appears to be justifiable without many of the restrictions of some of the special purpose models. Furthermore, with the diffusivity described by an integral law such as (2.19) we can explicitly incorporate the most important property of a glassy polymer, namely the finite relaxation time implied by the slow (rather than instantaneous) response to changing conditions.

The system (2.15), (2.19) in all its generality is very formidable. However, in the present paper we are studying the main features of the transition from a dry polymer to a fully saturated one in the dual sorption mode and its relationship to the sigmoid sorption process. Even with the assumptions invoked in all the common models [1]–[16] detailed knowledge of $R(x, t, C, C_t, C_x)$ from a molecular or statistical-dynamical theory would be difficult to obtain. However, for our continuum mechanics model we need only observe that $R(x, t, C, C_t, C_x)$ should provide the kinetics incorporating the change from a dry polymer to a fully saturated one. Qualitatively there should be little difference from the simple assumption of the most commonly occurring bimolecular stationary form

$$R(x, t, C, C_t, C_x) = \mu C(k - C), \tag{2.20}$$

where μ represents the "strength" of the reaction and k represents the equilibrium concentration (or carrying capacity) towards which the reaction is driven.

Further generalization of (2.19) incorporating spatial correlation and a more general functional dependence is also possible, but the system (2.15), (2.19) seems quite satisfactory at its present level.

3. Traveling waves. The structure of the transition between different regimes (e.g., sigmoid behavior or the change from a Henry isotherm to a Langmuir isotherm in gaseous diffusion) and the role of the various terms in the equations of motion is very often nicely revealed by a study of traveling wave solutions. Even in more general

solutions transition zones in some appropriate scaled variables are often described by traveling waves. Thus, we shall first study traveling wave solutions.

We shall show the existence of traveling wave solutions of equations (2.15), (2.16), where we take

$$R(x, t, C, C_t, C_x) = \mu C(k - C), \qquad \mu, k > 0. \tag{3.1}$$

It will be convenient to treat this system in the nondimensional form

$$c_\tau = [(g(c) - w)c_\chi]_\chi + c(1 - c), \tag{3.2}$$

$$w_\tau = h(c)c_\tau - \beta(c)w, \tag{3.3}$$

where

$$c = \frac{C}{k}, \quad \tau = \mu k t, \quad \chi = \sqrt{\frac{\mu k}{G(0)}}\, x,$$

$$w = \frac{G(C) - D}{G(0)}, \quad g(c) = \frac{G(C)}{G(0)}, \quad f(c) = \frac{F(C)}{G(0)}, \tag{3.4}$$

$$\beta(c) = \frac{\alpha(C)}{\mu k}, \qquad h(c) = \frac{d}{dc}[g(c) - f(c)].$$

We seek *nonnegative* solutions of (3.2), (3.3) under the following hypotheses:

H-1. $\beta(0) > 0$.

H-2. $f(0) = g(0) = 1$.

H-3. $f(c)$, $g(c)$, and $\beta(c)$ are monotonically nondecreasing and $h(c) \geqq 0$ for $c \geqq 0$.

H-4. $f'(c)$, $g'(c)$, and $\beta(c)$ satisfy a Lipschitz condition for $c \geqq 0$.

The requirement of nonnegativity on c simply reflects the fact that physically the concentration C is always nonnegative. Conditions H-1 to H-3 are a consequence of the following observations: The diffusion coefficient should be positive so that the flow is from higher to lower concentrations. This coupled with the interpretation of $F(C)$ as an instantaneous diffusion coefficient and $G(C)$ as an equilibrium diffusion coefficient imply $G(C) \geqq F(C) > 0$. It is experimentally noted that relaxation gets faster as concentration increases, so that $\alpha(C)$ is monotonically nondecreasing. In a perfectly dry polymer, D should be constant which occurs if either $\alpha(0) = 0$ or if $F(0) = G(0)$; we use the latter. Finally, condition H-4 is a technical condition we need in our proofs; this is satisfied by all the functions used in practice.

Assume solutions of the form

$$c(\chi, \tau) = c(\xi), \qquad w(\chi, \tau) = w(\xi), \tag{3.5}$$

where

$$\xi = -(\chi + a\tau), \tag{3.6}$$

and where a is the constant nondimensional velocity. Define $u = -dc/d\xi$. Then, (3.2), (3.3) become

$$\frac{dc}{d\xi} = -u,$$

$$\frac{d}{d\xi}[(g(c) - w)u] = -au + c(1 - c), \tag{3.7}$$

$$\frac{dw}{d\xi} = \frac{\beta(c)}{a} w - h(c)u.$$

We now study the system (3.7) in (c, u, w)-phase space.

The system (3.7) has two critical points given by

$$(c, u, w) = (0, 0, 0) \quad \text{and} \quad (c, u, w) = (1, 0, 0). \tag{3.8}$$

(If $\alpha(0) = 0$, then the w-axis is a singular line. Our results remain true in this case also, but the proof is more complicated. See Stanley [17] for details.) The existence of a (nonnegative) traveling wave solution with $c \to 0$ as $t \to -\infty$ and $c \to 1$ as $t \to \infty$ is equivalent to the existence of a trajectory (in $c \geqq 0$) of (3.7) which starts at $(1, 0, 0)$ as $\xi \to -\infty$ and terminates at $(0, 0, 0)$ as $\xi \to \infty$. Condition H-4 guarantees the (local) existence of unique solutions of all initial value problems away from the surface $w = g(c)$. Trajectories can intersect only at the critical points (away from this surface), and these critical points can be reached only as $\xi \to \pm\infty$. Linearization about each critical point serves to determine the behavior near the critical points.

Some feel for the geometry of our phase space can be obtained from the numerical examples of Figs. 1–3 in which a connector or lack of one is illustrated. These figures show solution curves of (3.7) projected onto the (u, c) and (w, c) planes. The letters $A, B, C, \cdots$ identify the different projections of the same curve. Initial values are taken on **U**, the unstable manifold defined in (3.17). In Figs. 1 and 2 a connector exists. In Figure 3 a connector does not exist since u and w do not go to zero as c does.

Near $(0, 0, 0)$ the linearized equations are

$$\begin{aligned} \dot{c} &= -u, \\ \dot{u} &= c - au, \\ \dot{w} &= -h(0)u + \frac{\beta(0)}{a}w, \end{aligned} \tag{3.9}$$

where the superscript dot denotes $d/d\xi$. This system has eigenvalues ν and eigenvectors

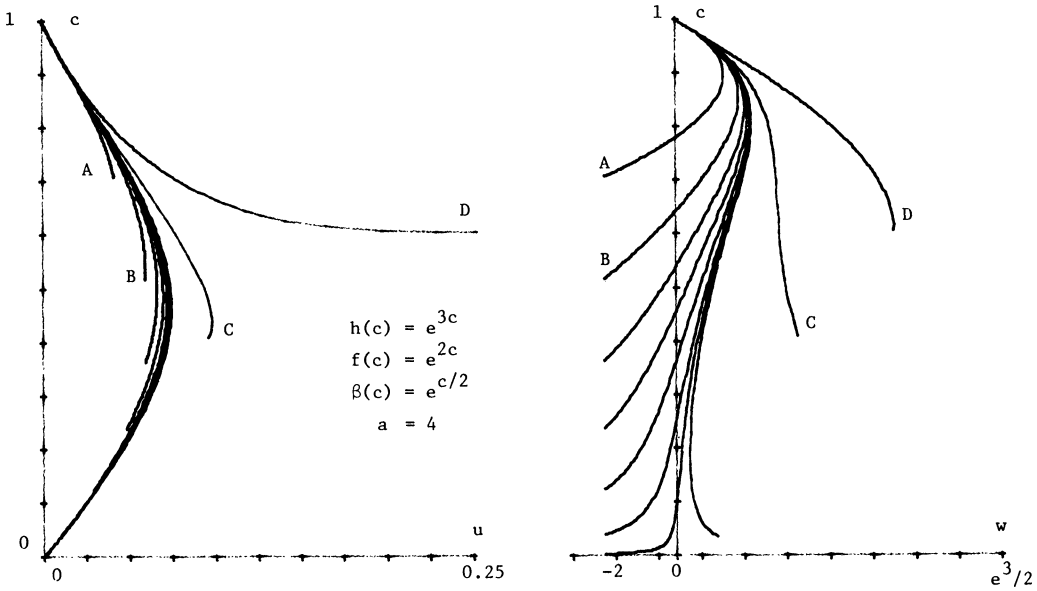

FIG. 1

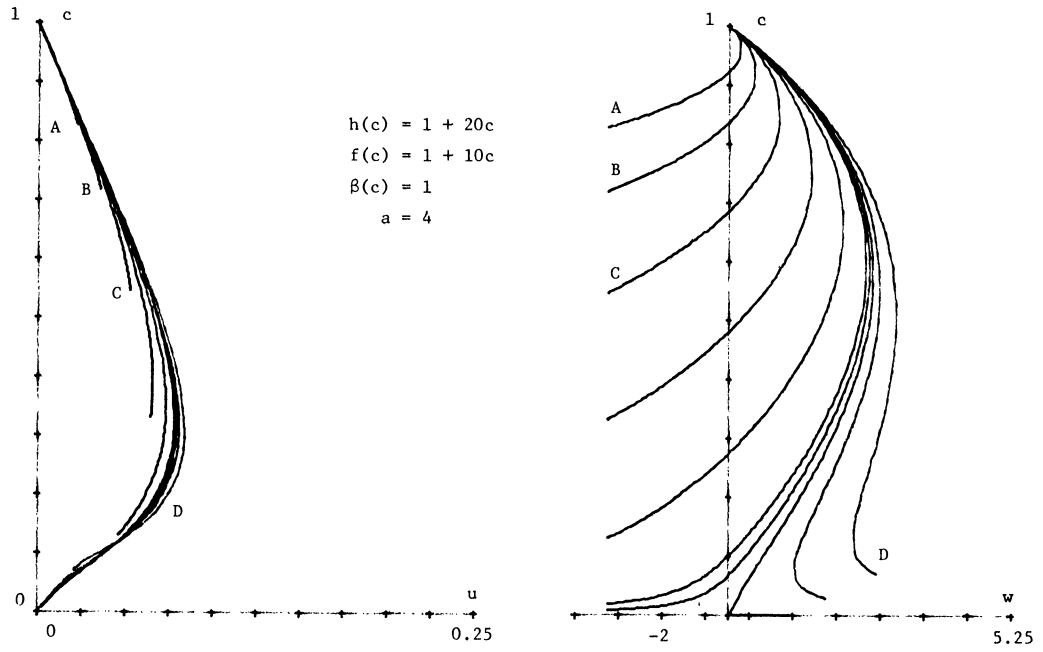

FIG. 2

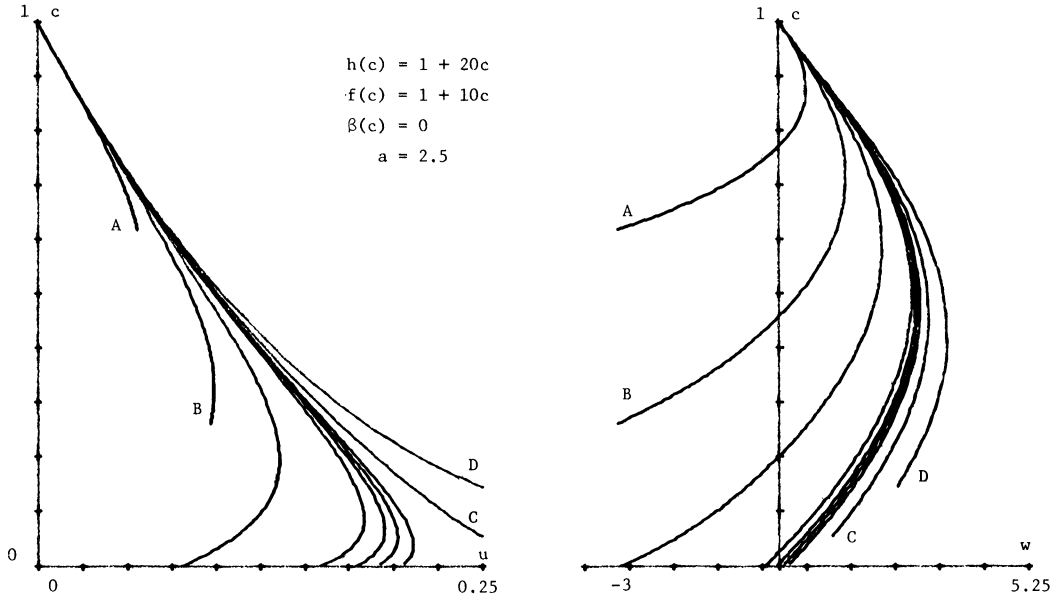

FIG. 3

$\mathbf{Y} \equiv (c, u, w)$ given by

$$\nu_0 = \frac{\beta(0)}{a}, \qquad \mathbf{Y}_0 = (0, 0, 1), \tag{3.10}$$

$$\nu_\pm = \frac{-a}{2} \pm \sqrt{\frac{a^2}{4} - 1}, \qquad \mathbf{Y}_\pm = \left(1, -\nu_\pm, \frac{\nu_\pm h(0)}{\nu_\pm - \nu_0}\right). \tag{3.11}$$

Near (1, 0, 0) the linearized equations are (with $c_1 = 1 - c$)

$$\begin{aligned} \dot{c}_1 &= u, \\ \dot{u} &= \frac{c_1}{g(1)} - \frac{au}{g(1)}, \\ \dot{w} &= -h(1)u + \frac{\beta(1)}{a} w, \end{aligned} \tag{3.12}$$

whose eigenvalues λ and eigenvectors $\mathbf{X} \equiv (c, u, w)$ are given by

$$\lambda_0 = \frac{\beta(1)}{a}, \qquad \mathbf{X}_0 = (0, 0, 1), \tag{3.13}$$

$$\lambda_\pm = \frac{-a \pm \sqrt{a^2 + 4g(1)}}{2g(1)}, \qquad \mathbf{X}_\pm = \left(1, \lambda_\pm, \frac{-h(1)\lambda_\pm}{\lambda_\pm - \lambda_0}\right). \tag{3.14}$$

Returning to the region near the origin, (0, 0, 0), we see that the linearized system behaves in different ways according to the size of a.

(i) $a \geqq 2$. There are two negative eigenvalues, ν_+ and ν_-, and one positive one, ν_0. Thus, there is a two-dimensional surface of trajectories approaching (0, 0, 0) and a pair of trajectories going away from (0, 0, 0). This is essentially the three-dimensional analogue of a saddle point in the phase-plane.

(ii) $-2 > a > 2$. There are two complex eigenvalues, $\nu_\pm$, and one real one, ν_0. This implies that the trajectories approaching or leaving the origin spiral around it. Furthermore, since the eigenvectors $Y_\pm$ are not in the $c = 0$ plane, these trajectories must enter the (unphysical) region $c < 0$.

(iii) $a \leqq -2$. There are two positive eigenvalues, $\nu_\pm$, and one negative one, ν_0. Thus, there is a two-dimensional surface of trajectories leaving the origin and a pair of trajectories approaching it.

Note that

$$c = 0, \quad u = 0, \quad w = w_0 e^{\beta(0)\xi/a}, \tag{3.15}$$

and

$$c = 1, \quad u = 0, \quad w = w_0 e^{\beta(1)\xi/a} \tag{3.16}$$

are solutions of (3.7) for any constant w_0. Thus, the w-axis and the line $c = 1$, $u = 0$ are trajectories leaving the critical points if $a > 0$ and approaching the critical points if $a < 0$. Since we are looking for a trajectory in $c \geqq 0$ which starts at (1, 0, 0) and terminates at (0, 0, 0), we can rule out cases (ii) and (iii). That is, case (ii) with wave speeds $-2 < a < 2$ violates the requirement that $c \geqq 0$, and case (iii) with $a \leqq -2$ is ruled out since the only trajectories approaching the origin do so along the *w-axis* and must come from $w = \pm\infty$ with c and u zero for all ξ. Therefore, if there exist acceptable traveling wave solutions, they must have $a \geqq 2$. We shall now demonstrate their existence. Note that even if $a \geqq 2$ there may not exist such solutions as we see from Fig. 3.

Since λ_0 and λ_+ are positive and λ_- is negative, then near (1, 0, 0) we have an unstable two-dimensional manifold of trajectories which has the form

$$\mathbf{U} \equiv \begin{pmatrix} 1-c \\ u \\ w \end{pmatrix} = m\mathbf{X}_0 + n\mathbf{X}_+ + o(|m| + |n|). \tag{3.17}$$

The major part of our proof consists of showing that for an appropriately chosen region with the two critical points on its boundary there is a family of trajectories on **U** near (1, 0, 0) inside this region such that at least one member of this family meets the critical point at the origin. We use a continuity argument.

Let R be the closed region defined by

$$R=\{(c, u, w): 0\leqq c\leqq 1, -\gamma\leqq w\leqq g(c)-f(c), 0\leqq u\}, \tag{3.18}$$

where γ is any positive constant. A sketch of the region R is given in Fig. 4. We first show that for large enough wave speeds a, solutions of (3.7) which start inside R on **U** near (1, 0, 0) satisfy $u<\mu c(1-c)$ so long as they remain inside R. Here μ is a positive constant.

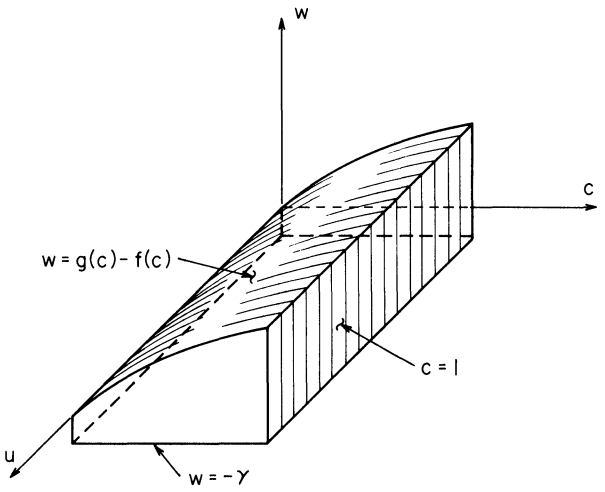

FIG. 4

Suppose that at $\xi=0$ we have a solution u such that

$$0<u<\mu c(1-c), \quad 0<c<1, \quad -\gamma<w<g(c)-f(c). \tag{3.19}$$

Then either (3.19) is satisfied for all $\xi\geqq 0$ which is what we want, or there exists a $\xi=s>0$ such that the trajectory touches or tries to cross the cylinder $u=\mu c(1-c)$ or leaves R through its boundary. If the trajectory stays in R, we must show that it cannot touch or cross $u=\mu c(1-c)$. If it does, at $\xi=s$ we have

$$u=\mu c(1-c), \quad 0<c<1, \quad -\gamma\leqq w\leqq g(c)-f(c). \tag{3.20}$$

We will show that $\mu>0$ can be chosen to contradict (3.20). Since $dc/d\xi=-u$, then c is monotonically decreasing for $\xi\in[0, s)$. Thus, in order for the trajectory to reach the cylinder $u=\mu c(1-c)$ at $\xi=s$, the slope du/dc of this trajectory must be less than the slope $(d/dc)[\mu c(1-c)]$ of the cylinder at $\xi=s$. This implies that at $\xi=s$

$$\frac{du}{d\xi}\geqq\frac{d}{d\xi}[\mu c(1-c)]=\mu(2c-1)u. \tag{3.21}$$

Upon combining (3.20), (3.21), and (3.7), we obtain

$$[(g(c)-w)(2c-1)-f'(c)c(1-c)]\mu^2+\left[a-\frac{w\beta(c)}{a}\right]\mu-1\leqq 0. \tag{3.22}$$

Clearly, for any $\mu > 0$ we can choose a value of a sufficiently large such that inequality (3.22) is violated. We now choose μ sufficiently large so that some part of the manifold **U** of (3.17) is contained in the new region W defined by

$$W \equiv \{(c, u, w): 0 \leqq c \leqq 1, 0 \leqq u \leqq \mu c(1-c), -\gamma \leqq w \leqq g(c) - f(c)\}. \tag{3.23}$$

A sketch of the region W is given in Fig. 5. A study of the derivatives of c, u, and w given by (3.7) shows that at some points on the boundary of W trajectories are

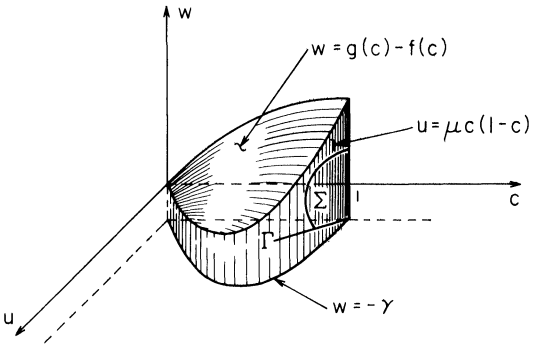

FIG. 5

leaving W. This leads us to define the immediate exit set W^- of W. W^- consists of the set of points in W where solutions of (3.7) immediately leave. More precisely, if $\mathbf{Y}_0 \equiv (c_0, u_0, w_0)$ is an initial value on the boundary ∂W of W for (3.7) and if $\mathbf{Y}(\xi, \mathbf{Y}_0)$ is the corresponding solution, then

$$W^- \equiv \{\mathbf{Y}_0 \in \partial W: \mathbf{Y}(\xi, \mathbf{Y}_0) \notin W \text{ for any } \xi > 0\}. \tag{3.24}$$

The behavior of trajectories near the boundary of W is summarized in Table 1.

TABLE 1
Behavior of trajectories near the boundary of W.

Faces		
$u = 0$	$\dot{u} > 0$	enter W
$w = g(c) - f(c)$	$\frac{dw}{dc} < \frac{d}{dc}[g(c) - f(c)], \dot{c} < 0$	leave W
$u = \mu c(1-c)$	$\frac{du}{dc} > \mu \frac{d}{dc}[c(1-c)], \dot{c} < 0$	enter W
$w = -\gamma$	$\dot{w} < 0$	leave W
Edges		
$c = 1, u = 0$	$\dot{c} = 0, \dot{u} = 0$	stay on this line
$w = g(c) - f(c), u = 0$	$\dot{w} > 0, \dot{c} = 0$	leave W
$w = g(c) - f(c), u = \mu c(1-c)$	$\frac{dw}{dc} < \frac{d}{dc}(g(c) - f(c)), \dot{c} < 0$	leave W
$w = -\gamma, u = \mu c(1-c)$	$\dot{w} < 0$	leave W
$c = 0, u = 0$	$\dot{c} = 0, \dot{u} = 0$	stay on this line
$w = -\gamma, u = 0$	$\dot{w} < 0$	leave W
Corners		
$c = 1, u = 0, w = -\gamma$	$\dot{w} < 0$	leave W
$c = 1, u = 0, w = g(1) - f(1)$	$\dot{c} = 0, \dot{w} > 0, \dot{u} = 0$	leave W
$c = 0, u = 0, w = 0$		critical point
$c = 0, u = 0, w = -\gamma$	$\dot{w} < 0$	leave W

We can take γ small enough so that the two-dimensional manifold **U** of (3.17) intersects the plane $w = -\gamma$ near (1, 0, 0) in a curve Γ. Since the trajectory $c = 1$, $u = 0$ is on **U** and is represented by taking $n = 0$ in (3.17), a circle of sufficiently small radius on **U** about (1, 0, 0) will intersect both the curve Γ and the line $c = 1$, $u = 0$. Define Σ as the part of this circle which lies in W and has one endpoint on Γ and the other endpoint on a trajectory with $c < 1$ which exits W through the face $w = g(c) - f(c)$.

We shall show that there is a solution of (3.7) starting on Σ which stays inside W until $c = 0$ and thus terminates in the critical point at (0, 0, 0) as $\xi \to \infty$. This is accomplished by showing that a condition in the following theorem of Wazewski is violated:

WAZEWSKI'S THEOREM. *Consider the differential equation*

$$\frac{dy}{dt} = F(y), \quad y \in \mathbb{R}^n, \tag{3.25}$$

where $F(y)$: $\mathbb{R}^n \to \mathbb{R}^n$ is continuous and satisfies a Lipschitz condition. Let $y(t; y_0)$ be the unique solution of (3.25) *satisfying $y(0; y_0) = y_0$. Given $W \subseteq \mathbb{R}^n$, let W^- denote the immediate exit set of W. For $\Sigma \subseteq W$ define Σ^0 to be those points $y_0 \in \Sigma$ where $y(t; y_0)$ is not in W for some finite $t > 0$. For $y_0 \in \Sigma^0$, define $T(y_0) = \sup \{t: y(\tau; y_0) \subseteq W \text{ for all } \tau \in [0, t]\}$. $T(y_0)$ is the exit time for a solution of* (3.25) *starting at y_0. Suppose that*

(i) *If $y_0 \in \Sigma$ and $y(t; y_0) \subseteq$ the closure of W, then $y(t; y_0) \subseteq W$.*

(ii) *If $y_0 \in \Sigma$ and $y(t; y_0)$ is in W but not in W^-, then there is an open set in W about $y(t; y_0)$ which is disjoint from W^-.*

(iii) *$\Sigma = \Sigma^0$, Σ is compact and intersects any trajectory of* (3.25) *at most once.*

Then, the mapping $y(T(y_0); y_0)$ from Σ to its image on W^- is one-to-one, continuous, and has a continuous inverse.

This version of Wazewski's theorem is due to Dunbar [18] who used it in a similar way.

Roughly speaking, the theorem says that, if hypotheses (i) and (ii) are satisfied, and if all trajectories through Σ exit W in finite time, then the image Σ^- of these trajectories on the exit set W^- is a continuous curve. From the definition of Σ we know that the trajectory through one endpoint exits W through the face $w = g(c) - f(c)$ while the trajectory through the other endpoint exits W through the face $w = -\gamma$. Since these two faces are disjoint in the exit set W^-, the curve Σ^- cannot be continuous. Thus, if we show that hypotheses (i) and (ii) are satisfied, we can conclude that there must exist a trajectory through Σ on which it takes infinite time to reach the boundary. Since c is monotonically decreasing, this curve must approach the other critical point at (0, 0, 0) as $\xi \to \infty$.

Since W is closed, condition (i) is satisfied trivially. To show that condition (ii) is satisfied we must show that no trajectory crossing Σ can reach that part of the boundary of W which is not in W^- in finite time. Referring to Table 1, we see that the part of the boundary of W which is not in W^- contains

(i) both critical points, (0, 0, 0) and (1, 0, 0),

(ii) the trajectories along $c = 1$, $u = 0$ and along $c = 0$, $u = 0$,

(iii) the faces $u = 0$ and $u = \mu c(1 - c)$.

No trajectory can reach a critical point in finite time, nor do trajectories intersect away from critical points. This implies that, since Σ does not contain any point on the lines $c = 1$, $u = 0$ and $c = 0$, $u = 0$, no trajectory crossing Σ can reach these lines in finite time. Trajectories are entering W on the faces $u = 0$ and $u = \mu c(1 - c)$ so that no trajectory can approach them from inside. Thus, a solution of (3.7) with initial value on Σ is in the interior of W until it reaches W^-, and condition (ii) holds.

We have shown that the conclusion of Wazewski's theorem does not hold, yet conditions (i) and (ii) do hold. It must be, therefore, that condition (iii) does not hold. Since Σ is compact, and trajectories intersect it at most once, then $\Sigma \neq \Sigma^0$. Thus, there is at least one trajectory crossing Σ which never leaves W. From the previous paragraph, this trajectory remains in the interior of W for all finite time. So $u > 0$ and (3.7) imply that c is monotonically decreasing, and this trajectory must approach the origin.

We conclude that for large enough values of the wavespeed a, there is always at least one trajectory of (3.7) going from the critical point at $(1, 0, 0)$ to the critical point at the origin. This connecting trajectory is a traveling wave front solution of (3.2)–(3.3).

4. A constructive approximation. In the case where k is small we can construct and prove the convergence of an interative approximation which exhibits the analytic structure of the traveling wave solutions. Furthermore, we need not assume that the wave speed is large. We shall follow the method of Kopell and Howard [19] who also constructed a three-dimensional connector for a similar problem.

Thus, we again consider (2.15), (2.16) with $R(x, t, C, C_t, C_x)$ given by (3.1). Define

$$\varepsilon = \frac{\mu k}{\alpha(k)}, \quad X = \sqrt{\frac{\alpha(k)}{G(k)}}x, \quad T = \alpha(k)t, \tag{4.1}$$
$$V = \frac{\mu(C-k)}{\alpha(k)}, \qquad W = \frac{G(C)-D}{G(k)},$$

so that (2.15), (2.16), (3.1) become

$$V_T = [(\Gamma(V) - W)V_X]_X + V(V+\varepsilon), \tag{4.2}$$

$$W_T = H(V)V_T - B(V)W, \tag{4.3}$$

where

$$\Gamma(V) = \frac{G(C)}{G(k)}, \quad H(V) = \frac{d}{dv}\left[\frac{G(C)-F(C)}{G(k)}\right], \quad B(V) = \frac{\alpha(C)}{\alpha(k)}. \tag{4.4}$$

We seek nonnegative traveling wave solutions of (4.2), (4.3) assuming only that $\alpha(0) > 0$ and $F(0) = G(0)$. Thus, assume that

$$V(X, T) = V(s), \qquad W(X, T) = W(s), \tag{4.5}$$

where

$$s = X + AT. \tag{4.6}$$

Note that $A = (\sqrt{G(0)\varepsilon/G(k)})a$, where a is the velocity of § 3. Define $U = dV/ds$, and then (4.2), (4.3) become

$$\frac{dV}{ds} = U,$$
$$\frac{d}{ds}[(\Gamma(V) - W)U] = AU + V(V+\varepsilon), \tag{4.7}$$
$$\frac{dW}{ds} = H(V)U - \frac{B(V)W}{A}.$$

This system has two critical points at

$$(V, U, W) = (0, 0, 0) \quad \text{and} \quad (V, U, W) = (-\varepsilon, 0, 0),$$

and as $\varepsilon \to 0$, the two critical points coalesce.

With the change of variables

$$\begin{aligned} U &= \varepsilon^2 Z_2, & W &= \frac{\varepsilon^2 H(0) Z_2}{A + 1/A} + \varepsilon^2 Z_3, \\ V &= \varepsilon Z_1 + \frac{\varepsilon^2 Z_2}{A}, & t &= \frac{\varepsilon s}{A}, \end{aligned} \tag{4.8}$$

the system (4.7) becomes

$$\begin{aligned} \frac{dZ_1}{dt} &= -Z_1(1+Z_1) - \varepsilon\left[\frac{\phi}{A} - \frac{d\psi}{dt}\right], \\ \varepsilon\frac{dZ_2}{dt} &= A^2 Z_2 + AZ_1(1+Z_1) + \varepsilon\left[\phi - \frac{d\psi}{dt}\right], \\ \varepsilon\frac{dZ_3}{dt} &= AH(V)Z_2 - B(V)Z_3 - \varepsilon\frac{AH(0)}{A^2+1}\frac{dZ_2}{dt} + \varepsilon^2\frac{AH(0)B(V)}{A^2+1}Z_2, \end{aligned} \tag{4.9}$$

where

$$\begin{aligned} \phi &= Z_2\left(1 + 2Z_1 + \frac{\varepsilon}{A}Z_2\right), \\ \psi &= Z_2\left[\Gamma(V) - \Gamma(0) - \varepsilon^2\frac{AH(0)Z_2}{A^2+1} - \varepsilon^2 Z_3\right]. \end{aligned} \tag{4.10}$$

If $\varepsilon = 0$, the solution of (4.9) is given by

$$\begin{aligned} Z_1 &= \frac{1}{2}\left(\tanh\frac{t}{2} - 1\right), \\ Z_2 &= \frac{1}{4A}\operatorname{sech}^2\frac{t}{2}, \\ Z_3 &= \frac{-AH(0)}{A^2+1}\operatorname{sech}^2\frac{t}{2}, \end{aligned} \tag{4.11}$$

where we have chosen the constant of integration so that $Z_1(0) = \frac{1}{2}$. The vector (Z_1, Z_2, Z_3) of (4.11) is the lowest order approximation to the trajectory we are seeking; it has the typical hyperbolic tangent structure describing the transition between two states.

Define $\eta(t)$ by

$$Z_1 = \frac{1}{2}\left(\tanh\frac{t}{2} - 1\right) + \varepsilon\eta(t). \tag{4.12}$$

System (4.9) is then equivalent to

$$\eta(t)=\frac{1}{A}\psi(t)+\left(\operatorname{sech}^2\frac{t}{2}\right)\left\{\frac{-1}{A}\psi(0)-\int_0^t\left[\left(\cosh^2\frac{s}{2}\right)\left(\varepsilon^2\eta(s)+\frac{\phi(s)}{A}\right)+\frac{1}{2A}\psi(s)\sinh s\right]ds\right\},$$

(4.13)

$$Z_2(t)=-\psi(t)+\frac{1}{\varepsilon}\int_t^\infty e^{A^2(t-s)/\varepsilon}\left[\frac{A}{4}\operatorname{sech}^2\frac{s}{2}+\rho(s)\right]ds,$$

$$Z_3(t)=\frac{AH(0)}{A^2+1}\psi(t)+\frac{1}{\varepsilon}\int_{-\infty}^t e^{(s-t)/\varepsilon}\left[\frac{A^2H(0)}{4(A^2+1)}\operatorname{sech}^2\frac{s}{2}+\Omega(s)\right]ds,$$

where

$$\rho(t)=A\psi(t)-\varepsilon\eta(t)\left[\tanh\frac{t}{2}+\varepsilon\eta(t)\right], \tag{4.14}$$

$$\begin{aligned}\Omega(t)=&[(H(V)-H(0))(A^2+1)-H(0)(B(V)-1)]\frac{A}{A^2+1}Z_2\\&-[H(V)-H(0)]Z_3+\varepsilon\phi(t)-\frac{AH(0)}{A^2+1}\psi(t).\end{aligned} \tag{4.15}$$

Equations (4.13) form the basis for the following iteration scheme:

$$\begin{aligned}&\eta^{(0)}(t)\equiv 0,\\&Z_2^{(0)}(t)=\frac{A}{4}\int_0^\infty e^{-A^2\theta}\operatorname{sech}^2\left(\frac{t+\varepsilon\theta}{2}\right)d\theta,\\&Z_3^{(0)}(t)=\frac{A^2H(0)}{4(A^2+1)}\int_{-\infty}^0 e^{\theta}\operatorname{sech}^2\left(\frac{t+\varepsilon\theta}{2}\right)d\theta,\end{aligned} \tag{4.16}$$

$$\eta^{(n+1)}(t)=\frac{1}{A}\psi^{(n)}(t)-\left(\operatorname{sech}^2\frac{t}{s}\right)\left\{\frac{1}{A}\psi^{(n)}(0)+\int_0^t\left[\left(\cosh^2\frac{s}{2}\right)\left(\frac{\phi^{(n)}(s)}{A}+\varepsilon^2\eta^{(n)}(s)\right)+\frac{1}{2A}\psi^{(n)}(s)\sinh s\right]ds\right\}, \tag{4.17}$$

$$Z_2^{(n+1)}(t)=Z_2^{(0)}(t)-\psi^{(n)}(t)+A\int_0^\infty e^{-A^2\theta}\rho^{(n)}(t+\varepsilon\theta)\,d\theta,$$

$$Z_3^{(n+1)}(t)=Z_3^{(0)}(t)+\frac{AH(0)}{A^2+1}\psi(t)+\int_{-\infty}^0 e^{\theta}\Omega(s+\varepsilon\theta)\,d\theta.$$

We will show that as $n\to\infty$, the iterates $(\eta^{(n)}(t), Z_2^{(n)}(t), Z_3^{(n)}(t))$ converge to a solution of (4.13) when ε is small and $|A|\gg\varepsilon^{1/3}$ and that this solution approaches the point $(\eta, Z_2, Z_3)=(0,0,0)$ as $t\to\pm\infty$.

First, we show that each iterate is bounded for ε sufficiently small and $|A|\gg\varepsilon^{1/3}$. Since $0<\operatorname{sech}^2(t/2)<1$,

$$|\eta^{(0)}(t)|=0,\quad |Z_2^{(0)}(t)|<\frac{1}{4A}<L,\quad |Z_3^{(0)}(t)|<\frac{A^2H(0)}{4(A^2+1)}<M, \tag{4.18}$$

where L and M simply denote upper bounds for $|Z_2^{(0)}(t)|$ and $|Z_3^{(0)}(t)|$, respectively. Now, (4.10) and (4.12) imply that

$$\phi(t) = Z_2 \tanh\frac{t}{2} + \varepsilon Z_2\left(\eta + \frac{1}{A}Z_2\right), \tag{4.19}$$

so that if $|Z_2(t)| < 2L$, then

$$\left|\operatorname{sech}^2\frac{t}{2}\int_0^t Z_2(s)\tanh\frac{s}{2}\cosh^2\frac{s}{2}\,ds\right| < 2L. \tag{4.20}$$

Furthermore, since $\Gamma(V)$, $H(V)$ and $B(V)$ are analytic near $V(0)$, then (4.8), (4.10) and (4.15) imply that

$$\begin{aligned}
&\psi(t) = \varepsilon\Gamma'(0)Z_1Z_2 + O(\varepsilon^2),\\
&\Omega(t) = \varepsilon\left\{[H'(0)(A^2+1) - H(0)(B'(0)-\Gamma'(0))]\frac{AZ_2}{A^2+1} - H'(0)Z_3\right\}Z_1 + O(\varepsilon^2),\\
&\rho(t) = \varepsilon A\Gamma'(0)Z_1Z_2 - \varepsilon\eta(t)\tanh\frac{t}{2} + O(\varepsilon^2).
\end{aligned} \tag{4.21}$$

Let ε be sufficiently small such that if $|\eta| < 4L/A$, $|Z_2| < 2L$ and $|Z_3| < 2M$ for all t, then

$$\begin{aligned}
&\left|\frac{1}{A}\psi(t) - \left(\operatorname{sech}^2\frac{t}{2}\right)\right.\\
&\quad\cdot\left\{\frac{1}{A}\psi \qquad {}^{t}\left[\left(\cosh^2\frac{s}{2}\right)\left(\frac{\varepsilon}{A}Z_2(s)\left(\eta(s) + \frac{1}{A}Z_2(s)\right) + \xi^2\eta^2(s)\right)\right.\right.\\
&\qquad\qquad\qquad\qquad\left.\left. + \frac{1}{2A}\psi(s)\sinh s\right]ds\right\}\Bigg| < \frac{2L}{A},
\end{aligned} \tag{4.22}$$

$$\left|\psi(t) - A\int_0^\infty e^{-A^2\theta}\rho(t+\varepsilon\theta)\,d\theta\right| < L,$$

$$\left|\frac{AH(0)}{A^2+1}\psi(t) + \int_{-\infty}^0 e^{\theta}\Omega(s+\varepsilon\theta)\,d\theta\right| < M.$$

Then, $|\eta^{(0)}(t)| = 0 < 4L/A$, $|Z_2^{(0)}(t)| < 2L$, $|Z_3^{(0)}(t)| < 2M$, and (4.18), (4.20) and (4.22) imply that

$$|\eta^{(n)}(t)| < \frac{4L}{A}, \quad |Z_2^{(n)}(t)| < 2L, \quad |Z_3^{(n)}(t)| < 2M, \tag{4.23}$$

so that the iterates are uniformly bounded.

Using the uniform bounds, we next show that each iterate tends to zero as $t \to \pm\infty$. We present only the calculation for $t \to -\infty$; the case $t \to +\infty$ is similar. We need the preliminary result that if $\mathcal{F}(t)$ is bounded for all t, and if $\mathcal{F}(t) \sim bt^k e^t$ as $t \to -\infty$, where

b is a constant and $k>0$, then as $t\to-\infty$

$$\int_0^\infty e^{-A^2\theta}\,\mathcal{F}(t+\varepsilon\theta)\,d\theta\sim\frac{b}{A^2-\varepsilon}t^k e^k, \tag{4.24}$$

$$\int_t^0 \mathcal{F}(t)\sinh t\,dt\sim\frac{-b}{2(k+1)}t^{k+1}, \tag{4.25}$$

$$\int_t^0 \mathcal{F}(t)\cosh t\,dt\sim\frac{b}{2(k+1)}t^{k+1}, \tag{4.26}$$

$$\int_t^0 \mathcal{F}(t)\,dt\sim bt^k e^t, \tag{4.27}$$

$$\int_{-\infty}^0 e^\theta\,\mathcal{F}(t+\varepsilon\theta)\,d\theta\sim\frac{bt^k e^t}{1+\varepsilon}. \tag{4.28}$$

Note that (4.24) is valid only if $A^2>\varepsilon$; the integral is unbounded if $A^2\leqq\varepsilon$. Using (4.24)–(4.28) and the fact that $\operatorname{sech}^2(t/2)\sim 4e^t$ as $t\to-\infty$, we find immediately that as $t\to-\infty$,

$$\eta^{(0)}(t)\sim 0,\quad Z_2^{(0)}(t)\sim\frac{A}{A^2-\varepsilon}e^t,\quad Z_3^{(0)}(t)\sim\frac{A^2H(0)}{(1+\varepsilon)(A^2+1)}e^t. \tag{4.29}$$

Then, using (4.29) in (4.17), we obtain that as $t\to-\infty$,

$$\begin{aligned}
&\eta^{(1)}(t)\sim\frac{-\Gamma(-\varepsilon)}{A^2-\varepsilon}te^t,\\
&Z_2^{(1)}(t)\sim\frac{A}{(A^2-\varepsilon)^2}[A^2-\varepsilon\Gamma(-\varepsilon)]e^t,\\
&Z_3^{(1)}(t)\sim A\left[\frac{AH(0)}{(A^2+1)H(0)}+O(\varepsilon)\right]e^t.
\end{aligned} \tag{4.30}$$

By induction it can then be shown that as $t\to-\infty$

$$\begin{aligned}
&\eta^{(n+1)}(t)\sim(\text{constant})\frac{\varepsilon^{2n}t^{n+1}e^t}{(n+1)!},\\
&Z_2^{(n+1)}(t)\sim(\text{constant})\frac{\varepsilon^{2n+1}t^n e^t}{n!},\\
&Z_3^{(n+1)}(t)\sim(\text{constant})\frac{\varepsilon^{2n-2}t^{n-1}e^t}{(n-1)!}.
\end{aligned} \tag{4.31}$$

Therefore, $(Z_1^{(n)}(t), Z_2^{(n)}(t), Z_3^{(n)}(t))$ approaches the critical point $(-1, 0, 0)$ as $t\to-\infty$. In a similar manner we obtain that these iterates tend to the other critical point $(1, 0, 0)$ as $t\to+\infty$.

Finally, we show that the iterates converge to a solution of (4.13) for ε sufficiently small and $|A|\gg\varepsilon^{1/3}$. Define the norm

$$\|\chi(t)\|\equiv\sup_{-\infty<t<\infty}|\chi(t)|. \tag{4.32}$$

Then,

$$\|\eta^{(n+1)}+\eta^{(n)}\|<\left(\frac{1}{A}+\frac{6\varepsilon L}{A^2}\right)\|Z_2^{(n)}-Z_2^{(n-1)}\|$$

$$+\frac{\varepsilon}{A}[6\varepsilon^2 L\|\eta^{(n)}-\eta^{(n-1)}\|+d_{12}\|Z_2^{(n)}-Z_2^{(n-1)}\|+6L\|Z_2^{(n)}-Z_3^{(n-1)}\|], \tag{4.33}$$

$$\|Z_2^{(n+1)}-Z_2^{(n)}\|<\frac{8\varepsilon L}{A}\|\eta^{(n)}-\eta^{(n-1)}\|$$

$$+\varepsilon[d_{21}\|\eta^{(n)}-\eta^{(n-1)}\|+d_{22}\|Z_2^{(n)}-Z_2^{(n-1)}\|+4L\|Z_3^{(n)}-Z_3^{(n-1)}\|], \tag{4.34}$$

$$\|Z_3^{(n+1)}-Z_3^{(n)}\|<\varepsilon[d_{31}\|\eta^{(n)}-\eta^{(n-1)}\|+d_{32}\|Z_2^{(n)}-Z_2^{(n-1)}\|+d_{33}\|Z_3^{(n)}-Z_3^{(n-1)}\|]. \tag{4.35}$$

Here the d_{ij} are constants which are $O(1)$ in both A and ε. If we iterate once on the index, the resulting relations are

$$\|\eta^{(n+1)}-\eta^{(n)}\|<\frac{8\varepsilon L}{A^2}\left(1+\frac{6\varepsilon L}{A}\right)\|\eta^{(n-1)}-\eta^{(n-2)}\|+\frac{6\varepsilon^3 L}{A^2}\|Z_2^{(n-1)}-Z_2^{(n-2)}\|$$

$$+\frac{\varepsilon}{A}(C_{11}\|\eta^{(n-1)}-\eta^{(n-2)}\|+C_{12}\|Z_2^{(n-1)}-Z_2^{(n-2)}\|$$

$$+C_{13}\|Z_3^{(n-1)}-Z_3^{(n-2)}\|), \tag{4.36}$$

$$\|Z_2^{(n+1)}-Z_2^{(n)}\|<\left\{\frac{8\varepsilon L}{A^2}\left(1+\frac{6\varepsilon L}{A}+\frac{\varepsilon}{A}d_{12}\right)+\frac{\varepsilon}{A}C_{22}\right\}\|Z_2^{(n-1)}-Z_2^{(n-2)}\|$$

$$+\frac{\varepsilon^2 L}{A}C_{21}\|\eta^{(n-1)}-\eta^{(n-2)}\|+\left(\frac{\varepsilon L}{A}\right)^2 C_{23}\|Z_3^{(n-1)}-Z_3^{(n-2)}\|, \tag{4.37}$$

$$\|Z_3^{(n+1)}-Z_3^{(n)}\|<\frac{\varepsilon}{A}d_{31}\|Z_2^{(n-1)}-Z_2^{(n-2)}\|$$

$$+\frac{\varepsilon^2}{A}\{C_{31}\|\eta^{(n-1)}-\eta^{(n-2)}\|+C_{32}\|Z_2^{(n-1)}-Z_2^{(n-2)}\|$$

$$+C_{33}\|Z_3^{(n-1)}-Z_3^{(n-2)}\|\}, \tag{4.38}$$

where c_{ij} are $O(1)$ constants.

Now, let

$$\mathbf{y}(t)=\begin{pmatrix}\eta(t)\\ Z_2(t)\\ Z_3(t)\end{pmatrix}, \tag{4.39}$$

and define

$$\|\mathbf{y}\|_0\equiv\max\{\|\eta\|,\|Z_2\|,\|Z_3\|\}. \tag{4.40}$$

If $|A|\gg\varepsilon^{1/3}$, we can take $L\ll\varepsilon^{-1/3}$, so that $\varepsilon L/A^2$ is small if ε is small. Then, by inspection

$$\|\mathbf{y}^{(n+1)}-\mathbf{y}^{(n)}\|_0<\left[\left(\frac{8\varepsilon L}{A^2}\right)\left(1+\frac{6\varepsilon L}{A}\right)+O\left(\frac{\varepsilon}{A},\left(\frac{\varepsilon L}{A}\right)^2\right)\right]\|\mathbf{y}^{(n-1)}-\mathbf{y}^{(n-2)}\|_0. \tag{4.41}$$

Thus, for ε sufficiently small,

$$\|\mathbf{y}^{(2n+1)}-\mathbf{y}^{(2n)}\|<\alpha\|\mathbf{y}^{(2n-1)}-\mathbf{y}^{(2n-2)}\|, \tag{4.42}$$

and

$$\|\mathbf{y}^{(2n+2)}-\mathbf{y}^{(2n+1)}\|<\alpha\|\mathbf{y}^{(2n)}-\mathbf{y}^{(2n-1)}\|, \tag{4.43}$$

where $0<\alpha<1$. By the usual contraction mapping arguments, our sequence converges to a solution of (4.13).

5. The penetrant front. A crude but effective way to determine the behavior of the progressing penetrant front due to the type of diffusion given by (1.1), (1.2) is to employ an integral averaging method (commonly called the Karman–Pohlhausen method). A description of the method for problems in fluid mechanics together with a bibliography may be found in Schlichting [20]. An excellent more modern account of the method together with extensive references and applications to problems in heat transfer is given by Goodman [21].

We introduce the quantity $\delta(t)$ called the penetration distance (or propagating concentration front). For $x>\delta(t)$ the polymer is at its equilibrium (i.e., initial) concentration, and there is no flux transferred beyond $x=\delta(t)$. Thus,

$$C=0 \quad \text{at } x=\delta(t), \tag{5.1}$$

$$DC_x=0 \quad \text{at } x=\delta(t). \tag{5.2}$$

It is important to note that for our problem the "signal speed" is infinite. That is, solutions have a finite value for all x for all positive t for any initial or boundary data. This is a consequence of the fact that the characteristic surfaces for parabolic equations are parallel to the spatial axes. For practical purposes and often as a basis for sophisticated approximation techniques one defines a diffusion front as the locus of points moving with a given concentration. Clearly, on our problem we proceed in the standard way to take the concentration field $C(x,t)$ to be zero for $x>\delta(t)$ *to within the accuracy of the approximation* or equivalently we define the front to be the locus of a given (presumably small) concentration.

To assess the effect of our diffusive operator we consider

$$C_t=(DC_x)_x, \qquad x>0, \quad t>0, \tag{5.3}$$

$$D_t=F'(C)C_t+\alpha(C)[G(C)-D], \qquad x>0, \quad t>0, \tag{5.4}$$

$$C(0,t)=C_0, \qquad t\geqq 0, \tag{5.5}$$

$$C(x,0)=0, \qquad x>0. \tag{5.6}$$

Here C_0 is a prescribed constant. The kinetic term R and variable boundary data can be incorporated, but this complicates the algebra without adding anything essential to our study. We will comment on this later.

Upon integrating (5.3) with respect to x from 0 to $\delta(t)$, and making use of (5.2), we obtain

$$\int_0^{\delta(t)} C_t\,dx=-[DC_x]\big|_{x=0}. \tag{5.7}$$

We now assume that $C(x,t)$ can be approximated by an Nth degree polynomial in x

with time-dependent coefficients. This approximation is required to satisfy the boundary condition (5.5) and the conditions (5.1) and (5.2) at the front $x = \delta(t)$. Thus,

$$C(x, t) = C_0 \sum_{n=2}^{N} k_n \left[1 - \frac{x}{\delta(t)}\right]^n \tag{5.8}$$

where

$$\sum_{n=2}^{N} k_n = 1. \tag{5.9}$$

By differentiation in (5.3) it is possible (21) to derive $(N-2)$ conditions which the constants $k_n (n = 2, \cdots, N)$ must satisfy in addition to (5.9). We thus obtain $(N-1)$ equations in $(N-1)$ unknowns for the k_n. We shall not need that information here.

We now find $\delta(t)$ by requiring (5.2) to be an approximation in the sense that (5.7) is satisfied. Upon substituting (5.8) into (5.7), we obtain

$$\lambda \frac{d\delta}{dt} - \frac{\nu D(0, t)}{\delta} = 0 \tag{5.10}$$

where

$$\lambda = \sum_{n=2}^{N} \frac{k_n}{n+1}, \qquad \nu = \sum_{n=2}^{N} n k_n. \tag{5.11}$$

The boundary condition (5.5) implies that $C_t(0, t) = 0$. Thus, upon evaluating (5.4) at $x = 0$, we obtain

$$D_t(0, t) + \alpha_0 D(0, t) = G_0, \tag{5.12}$$

where

$$\alpha_0 = \alpha(C_0), \qquad G_0 = G(C_0). \tag{5.13}$$

Thus,

$$D(0, t) = G_0 + (F_0 - G_0)\, e^{-\alpha_0 t}, \tag{5.14}$$

where $F_0 = D(0, 0) = F(C_0)$. Therefore, (5.10) and (5.14) yield the following equation for the motion of the penetrant front:

$$\lambda \frac{d\delta}{dt} - \frac{\nu[G_0 + (F_0 - G_0)\, e^{-\alpha_0 t}]}{\delta} = 0, \tag{5.15}$$

the exact solution of which (satisfying $\delta(0) = 0$) is

$$\delta^2(t) = \frac{\nu}{\lambda} G_0 t - \frac{\nu}{\lambda \alpha_0}(F_0 - G_0)\, e^{-\alpha_0 t} + \frac{\nu}{\lambda \alpha_0}(F_0 - G_0). \tag{5.16}$$

Clearly,

$$\delta^2(t) \sim \frac{\nu}{\lambda} F_0 t \quad \text{for small } t, \tag{5.17}$$

$$\delta^2(t) \sim \frac{\nu}{\lambda} G_0 t + \frac{\nu}{\lambda \alpha_0}(F_0 - G_0) \quad \text{for large } t. \tag{5.18}$$

Thus, (5.15) describes the motion of the penetrant front $x = \delta(t)$ and yields the transition (i.e., the sigmoid sorption curve) from the instantaneous diffusivity F_0 to

the equilibrium diffusivity G_0. Retaining the kinetic term R in our problem (5.3)–(5.6) requires no changes in our procedure. We obtain instead of (5.15) a more complicated first order equation which possesses the asymptotic solution (5.17), (5.18).

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